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SI GUBAIN 00148395562

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JPA 5-253544

**[Title of the Invention]**

**A method of manufacturing a sheet-like member having a deodorizing function**

**[Abstract]**

**[Object]**

The object of the present invention is retaining photocatalytic fine particles in a surface of a tile or the like so as to perform a sufficient deodorizing function.

**[Structure]**

A glaze layer 2 is coated onto the surface of a tile body 1. Next, solated anatase type  $\text{TiO}_2$  fine particles 3 as photocatalytic fine particles are applied onto the surface of the glaze layer 2 with a sprayer or the like. Next, the glaze layer 2 is heated so as to cause fusion thereto, and thereafter it is cooled and cured.

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**[What is claimed is:]**

1. A method of manufacturing a sheet-like member having a deodorizing function comprising the steps of:

forming a binder layer on a surface of a sheet-like member for constructing a wall surface, a floor surface, or a ceiling surface of a residential space;

spraying photocatalytic fine particles mainly comprised of anatase type  $\text{TiO}_2$  onto the surface of said binder layer so that a part of each particle is exposed from said binder layer, thereby allowing said particles to adhere;

causing fusion to said binder layer by heating in the range of from 300 °C to 850 °C; and

thereafter cooling said binder layer so as to cure.

2. A method of manufacturing a sheet-like member having a deodorizing function comprising the steps of:

forming a sheet by spraying photocatalytic fine particles mainly comprised of anatase type  $\text{TiO}_2$  onto a surface of a binder layer so that a part of each particle is exposed from said binder layer;

applying said sheet to a sheet-like member for constructing a wall surface, a floor surface, or a ceiling surface of a residential space;

causing fusion to said binder layer by heating in the range of from 300 °C to 850 °C; and

thereafter cooling said binder layer so as to cure.

3. A method of manufacturing a sheet-like member having a deodorizing function as defined in claim 1 or claim 2, wherein said sheet-like member is a tile and said binder layer is a glaze layer or a print layer.

**[Detailed Description of the Invention]****[0001]****[Field of Industrial Application]**

The present invention relates to a method of manufacturing a sheet-like member for constructing a wall surface or the like of a toilet or a kitchen, specifically a sheet-like member having a deodorizing function.

**[0002]****[Prior Art]**

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Anatase type  $\text{TiO}_2$  has been known as a photocatalyst which accelerates a deodorizing reaction when irradiated by ultraviolet radiation. Also, the present applicant has already proposed a method in which a raw material comprising photocatalytic fine particles kneaded into a binder is coated onto the surface of a member for constructing a wall surface of a residential space, thereafter is fired, and thereby a deodorizing function is provided to the wall surface.

[0003]

[Problem to be Solved by the Invention]

FIG. 11 is an enlarged cross-sectional view of a wall having a deodorizing function which is obtained by the above-mentioned method. A binder layer 101 is formed on the surface of a wall member 100 and photocatalytic fine particles 102 are completely buried in the binder layer 101. As a result, since the photocatalytic fine particles 102 cannot directly be irradiated by ultraviolet radiation, they cannot perform a sufficient catalytic function.

[0004]

[Means for Solving Problem]

In order to solve the above-mentioned problem, according to the first aspect of the present invention, there is provided a method comprising the steps of forming a binder layer on a surface of a tile or the like, spraying photocatalytic fine particles mainly comprised of anatase type  $\text{TiO}_2$  onto the surface of the binder layer so that a part of each particle is exposed from the binder layer and thereby allowing the particles to adhere, causing fusion to the binder layer by heating, and thereafter cooling the binder layer so as to cure.

[0005]

According to the second aspect of the present invention, there is provided a method comprising the steps of forming a sheet by spraying photocatalytic fine particles mainly comprised of anatase type  $\text{TiO}_2$  onto a surface of a binder layer so that a part of each particle is exposed from the binder layer, applying the sheet to a tile or the like, causing fusion to the binder layer by heating, and thereafter cooling the binder layer so as to cure.

[0006]

[Operation]

By spraying photocatalytic fine particles onto the surface of a non-fired binder

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layer with a sprayer or the like, it is possible to prevent the photocatalytic fine particles from being buried completely in the binder layer and make the particles adhere in a condition whereby a part of each particle is exposed from the binder layer.

[0007]

[Example]

Hereinafter, preferred embodiments of the present invention will be described with reference to the drawings.

FIG. 1 is a view showing a method of manufacturing a sheet-like member having a deodorizing function according to the present invention in process sequence and FIG. 2 is an enlarged cross-sectional view of a tile which is obtained by the method of the present invention. According to the present invention, first, a glaze layer 2 is coated onto the surface of a tile body 1 as a sheet-like member for constructing a wall surface, a floor surface, or a ceiling surface, as shown in FIG. 1(a). Next, solated anatase type  $\text{TiO}_2$  fine particles 3 as photocatalytic fine particles are applied onto the surface of the glaze layer 2 with a sprayer or the like, as shown in FIG. 1(b). Next, the glaze layer 2 is heated so as to cause fusion thereto, and thereafter it is cooled and cured, as shown in FIG. 1(c). It is also possible to make the  $\text{TiO}_2$  sol have a disinfecting effect by adding Cu, Ag, or the like thereto. As a method of such addition, for example,  $\text{CuSO}_4$  may be added to the  $\text{TiO}_2$  sol in a condition of adjusting to be around pH11 with an  $\text{NH}_3$  solution.

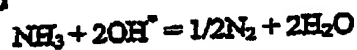
[0008]

As mentioned above, the  $\text{TiO}_2$  sol is sprayed onto the surface of the glaze layer 2, and thereby it is not buried completely therein. That is, as shown in FIG. 2, it is possible to retain the  $\text{TiO}_2$  fine particles 3 in the glaze layer 2 in a condition that a part of each  $\text{TiO}_2$  fine particle 3 enters into the glaze layer 2 and the other part is exposed.

[0009]

As a result of this, it is possible to irradiate ultraviolet rays directly upon the exposed part of the  $\text{TiO}_2$  fine particles 3 with a lamp which is fixed to a wall surface or the like (not shown in the drawing). When the  $\text{TiO}_2$  fine particles 3 are irradiated by ultraviolet radiation, adsorption water and positive holes of photocatalysts react so as to generate hydroxy group radicals ( $\text{OH}^\bullet$ ). The hydroxy group radicals and ammonia react as shown below, so as to conduct deodorizing.

[0010]



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## [0011]

FIGS. 3-7 show another embodiment. In the embodiment shown in FIG. 3, an ink layer 4 is formed on the surface of a glaze layer 2 by printing.  $\text{TiO}_2$  fine particles 3 are sprayed onto the surface of the ink layer 4 so that a part of each particle is exposed from the ink layer 4, and thereafter heating and cooling are conducted in the same manner as mentioned above.

## [0012]

In the embodiment shown in FIG. 4, a glaze layer 2 is formed on the surface of a release paper 5 through a soluble binder 6, a binder layer 7 is formed on the surface of the glaze layer 2,  $\text{TiO}_2$  fine particles 3 are sprayed onto the surface of the binder layer 7 so that a part of each particle is exposed from the binder layer 7, and thereby a sheet S is obtained. Then, the release paper 5 is removed, the sheet S is adhered to the surface of a tile body 1, and thereafter heating and cooling are conducted in the same manner as mentioned above. By preparing the sheet S further having a deodorizing function, it is possible to easily provide a deodorizing function to a tile or the like which is already in use.

## [0013]

In the embodiment shown in FIG. 5,  $\text{TiO}_2$  fine particles 3 are partly adhered to the surface of the ink layer 4 so as to form patterns. As a result of this, a decorative effect can be achieved. In this instance,  $\text{TiO}_2$  fine particles 3 may be formed the glaze layer 2.

## [0014]

In the embodiments shown in FIGS. 6 (a) and (b), concave portions are formed in a tile body 1 for preventing slip or the like. In the concave portions,  $\text{TiO}_2$  fine particles 3 are adhered with a glaze layer 2. In the case of forming concave portions, soil enters the concave portions and it is difficult to remove such soil. However, by retaining  $\text{TiO}_2$  fine particles 3 in the concave portions, such soil is decomposed and thereby it is possible to remove the soil with ease.

## [0015]

In the embodiment shown in FIG. 7, an ultraviolet-ray reflecting layer 8 is interposed between a glaze layer 2 and  $\text{TiO}_2$  fine particles 3. The ultraviolet-ray reflecting layer 8 is comprised of vapor deposition aluminum powder or magnesium oxide, for example. With this structure, it is possible to irradiate ultraviolet rays, which are transmitted through the  $\text{TiO}_2$  fine particles 3 once, upon the  $\text{TiO}_2$  fine particles 3 again, and thereby the catalytic effect can be improved.

## [0016]

FIG. 8 is a graph showing the results of the tests with respect to the relationship between the concentration of  $\text{CH}_3\text{SH}$  and the lapse time for each heat treatment (firing) temperature. In this graph,  $t_{1/10}$  shows the time required for obtaining the concentration of  $1/10$ , and the dotted line shows the case where no ultraviolet rays are irradiated. In addition, anatase type  $\text{TiO}_2$  particles having an average particle diameter of 100 Å are used. FIG. 9 is a graph showing the results of the tests with respect to the relationship between the heat treatment temperature and the odor removal ratio after 30 minutes. FIG. 10 is a graph showing the relationship between the concentration of  $\text{CH}_3\text{SH}$  and the lapse time at a temperature of 700 °C in the case where anatase type  $\text{TiO}_2$  having an average particle diameter of 500 Å are used.

[0017]

The following facts are shown in FIGS. 8, 9 and 10:

First, anatase type  $\text{TiO}_2$  performs as a catalyst under the presence of ultraviolet rays. Second, the catalytic effect thereof reaches its peak at a temperature of 700 °C. It is necessitated that the heat treatment temperature be in the range of 300 – 850 °C in order to obtain the odor removal ratio 50 % or more after 30 minutes. Apparently, this is because the desired level of catalytic activity to be enabled is hard to achieve at a heat treatment temperature less than 300 °C and the structure of  $\text{TiO}_2$  is transformed from anatase type to rutile type at a temperature exceeding 900 °C.

[0018]

[Effect of the Invention]

As mentioned above, according to the present invention, a binder layer is formed on the surface of a tile or the like and photocatalytic fine particles are sprayed onto the surface of the binder layer for allowing the particles to adhere thereto, or a sheet is formed by spraying photocatalytic fine particles onto the surface of a binder layer and the sheet is applied to a tile or the like. Then, fasion is caused to the binder layer by heating and thereafter the binder layer is cooled so as to cure. As a result of this, the photocatalytic fine particles can be retained in a condition that a part of each particle is exposed from the binder layer. Therefore, it is possible to irradiate ultraviolet rays directly upon the exposed parts of the particles and thereby the sufficient catalytic effect can be obtained.

[Brief Description of Drawings]

FIG. 1 is a view showing a method of manufacturing a sheet-like member having a deodorizing function according to the present invention in process sequence;

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FIG. 2 is an enlarged cross-sectional view of a tile which is obtained by the method of the present invention;

FIG. 3 is a cross-sectional view of a sheet-like member according to another embodiment;

FIG. 4 is a cross-sectional view of a sheet-like member according to another embodiment;

FIG. 5 is a cross-sectional view of a sheet-like member according to another embodiment;

FIG. 6 is a cross-sectional view of a sheet-like member according to another embodiment;

FIG. 7 is a cross-sectional view of a sheet-like member according to another embodiment;

FIG. 8 is a graph showing the relationship between the lapse time and the concentration of  $\text{CH}_3\text{SH}$  in a case of using anatase type  $\text{TiO}_2$  particles having an average particle diameter of 100 Å;

FIG. 9 is a graph showing the relationship between the heat treatment temperature and the odor removal ratio after 30 minutes;

FIG. 10 is a graph showing the relationship between the lapse time and the concentration of  $\text{CH}_3\text{SH}$  in a case of using anatase type  $\text{TiO}_2$  particles having an average particle diameter of 500 Å; and

FIG. 11 is a cross-sectional view of a sheet-like member having a deodorizing function according to a conventional manufacturing method.

[Explanations of numerals]

- 1 tile body
- 2 glaze layer
- 3  $\text{TiO}_2$  fine particle
- 4 ink layer
- 5 release paper.
- 8 ultraviolet-ray reflecting layer
- S sheet

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FIG. 1

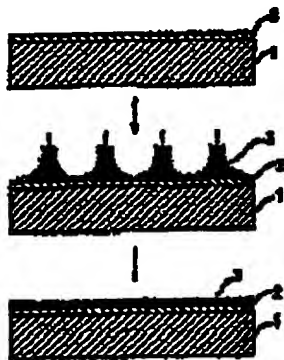


FIG. 2

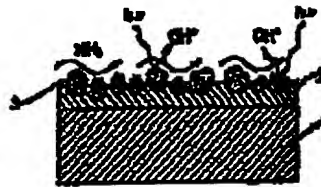


FIG. 3

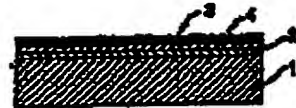


FIG. 4

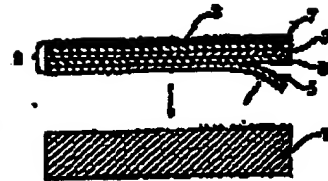
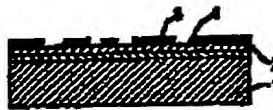


FIG. 5





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FIG. 6

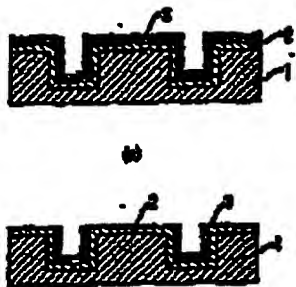


FIG. 7



FIG. 11

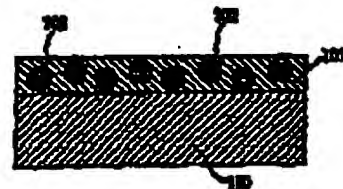


FIG. 8

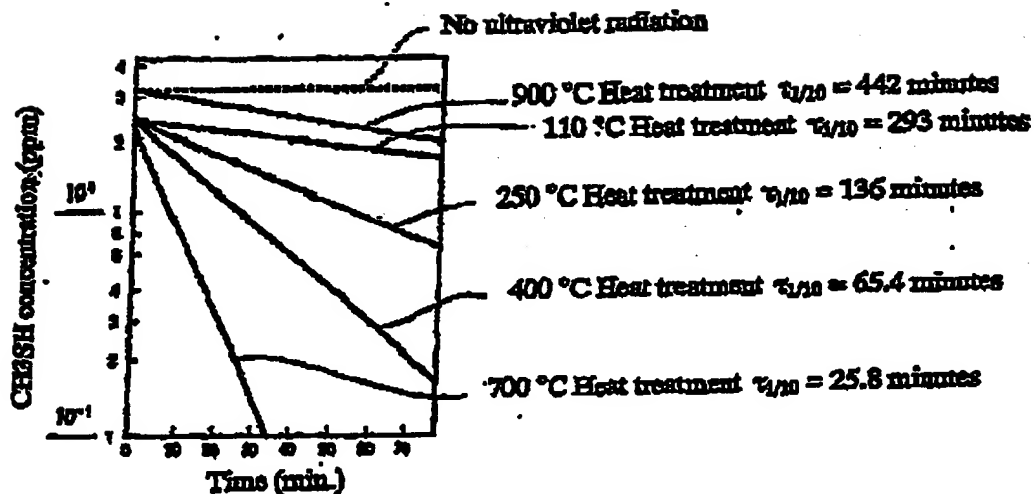
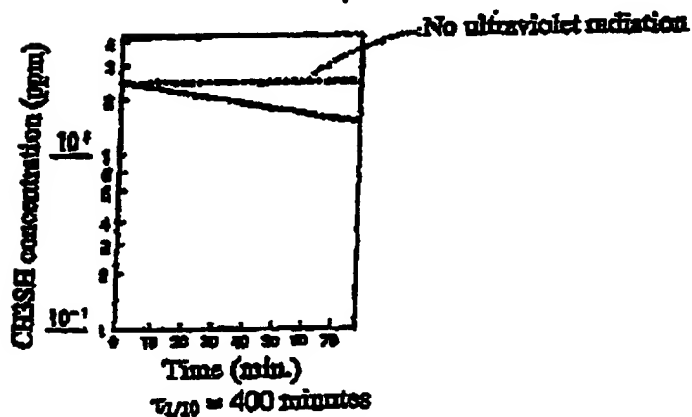


FIG. 10



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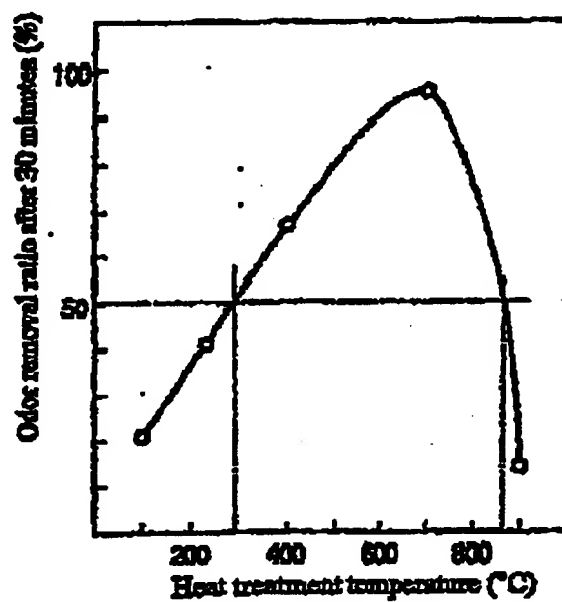
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FIG. 9



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L4 ANSWER 1 OF 1 WPINDEX (C) 2002 THOMSON DERWENT

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CROSS REFERENCE: 1998-234170 [21]; 1999-162164 [14]; 1999-162165 [14];  
1999-174990 [15]; 2000-415235 [35]; 2000-495510 [44];  
2000-495512 [44]; 2000-495513 [44]; 2000-495514 [44];  
2000-495515 [44]; 2000-495516 [44]; 2000-495517 [44];  
2000-495518 [44].

DOC. NO. NON-CPI: N1993-268462  
DOC. NO. CPI: C1993-153959

TITLE: Deodorising plate-shaped member prodn., for walls, etc. -  
by adhering photocatalyst particles to binder layer on  
plate, heating the binder layer and cooling.

DERWENT CLASS: D22 J01 L02 P34 P42 P73 Q44 Q45

PATENT ASSIGNEE(S): (TTOC) TOTO LTD

COUNTRY COUNT: 1

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JP 2667331	B2	19971027	(199748)		5	B05D007-24	

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E04C002-02; E04F013-08

#### BASIC ABSTRACT:

JP 05253544 A UPAB: 20000913

Prodn. comprises (a) forming a binder layer on the surface of a plate-shaped member for a wall, floor, or ceiling; (b) spraying adhering photocatalyst particles comprising mainly anatase type TiO<sub>2</sub> at and to the surface of the binder layer so that part of the particles are exposed from the binder layer; (c) heating the binder layer at 300 - 850 deg.C to melt it and (d) cooling the binder layer to solidify it.

Pref. the plate-shaped member comprises a tile, and the binder layer comprises a glaze or printed layer.

USE/ADVANTAGE - The plate-shaped member is used in a wall, floor or ceiling of a toilet or a kitchen. UV rays directly hit the exposed particles to activate the catalyst.

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FILE SEGMENT:

CPI GMPI

FIELD AVAILABILITY:

AB

MANUAL CODES:

CPI: D09-B; J01-E02; L02-D09